

Preparation of (η^6 -alkoxytriphenylene)tricarbonyl chromium(0) complexes

Mesomorphic properties of a disk-shaped chromium–arene complex

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Abstract

Novel (η^6 -hexaalkoxytriphenylene)Cr(CO)₃ complexes **9** with varying alkyl chain lengths (C₅H₁₁ to C₉H₁₉) have been prepared with the chromium tricarbonyl moiety being exclusively attached to one terminal aryl ring. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction showed that complexes **9a–d** displayed isotropic melting behavior. However, hexanonyloxy-substituted complex **9e** displayed a nematic N_D phase between 37° and 58°C. © 1998 Elsevier Science S.A.

Keywords: Chromium arene complex; Metallomesogen; Triphenylene; Nematic liquid crystal

1. Introduction

Although metallomesogens are known for a long time, research efforts dealing with these metal-containing liquid crystals have been intensified only recently [1–3]. One reason is that the combination of a metal complex with an organic liquid crystal often leads to compounds with unprecedented physical properties, which might be useful for potential applications in molecular electronics, electric or magnetic switches, or novel electric conducting materials. Despite the variability of both central metal, coordination number and geometry, and type of mesogenic ligand, some classes of metal complexes have only rarely been investigated. Among them are chromium arene complexes [1–3]. This is surprising, because chromium arene complexes can be easily prepared, they are mostly stable com-

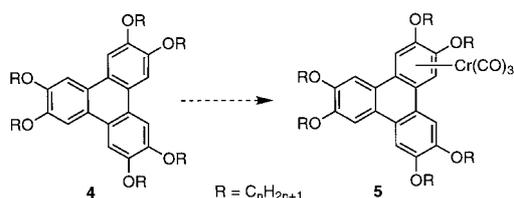
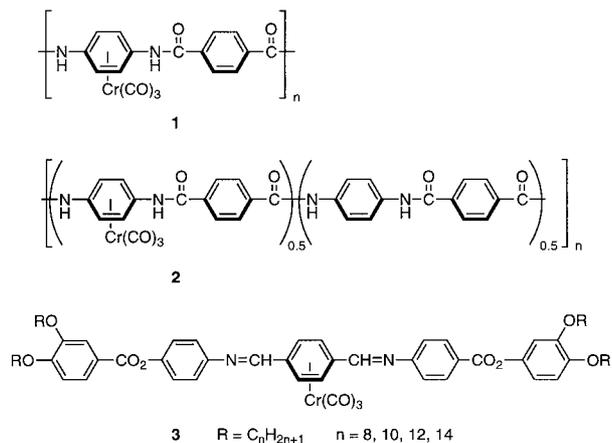
pounds and due to the enhanced stability of benzylic anions and cations, the increased electrophilicity and the steric shielding of one face of the aromatic ring by the bulky metal fragment, various applications of chromium arene complexes as steric and/or electronic templates have been developed in synthetic organic chemistry [4–8].^{2,3} To our knowledge only two examples of chromium arene complexes exhibiting mesomorphic behavior existed in the literature. As reported by Dembek π -complexed poly-*p*-phenylene terephthalamides **1**, **2** (Scheme 1) display nematic lyotropic textures when dissolved in 5% *N,N'*-dimethylacetamide [14–17]. Deschenaux studied calamitic 1,4-phenylene bisimine chromium tricarbonyl complexes **3**, which exhibited nematic and smectic C mesophases [18]. These results

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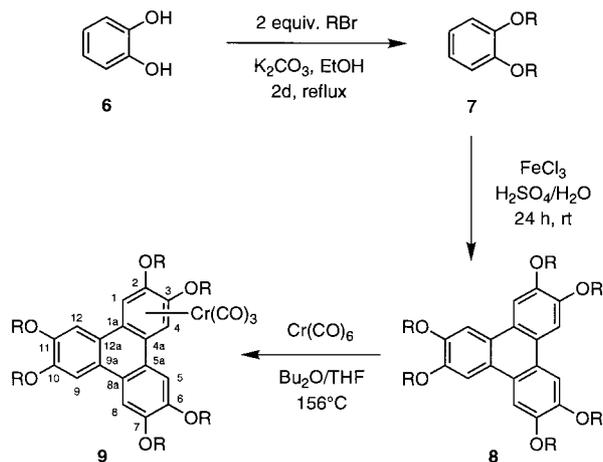
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² Recent examples of chromium arene complexes in radical reactions, see Refs. [9,10].

³ Chromium arene complexes as catalysts, see Refs. [11–13].



prompted us to search for discotic liquid crystals bearing a chromium arene moiety. We therefore investigated the change of the well-known mesomorphic properties



R	Yields [%]			
	7-9	7	8	9
C ₅ H ₁₁	a	97	42	71
C ₆ H ₁₃	b	99	31	99
C ₇ H ₁₅	c	90	29	86
C ₈ H ₁₇	d	94	23	71
C ₉ H ₁₉	e	92	26	89
C ₁₀ H ₂₁	f	99	25	---

Scheme 3.

Table 1
Phase transition temperatures for triphenylenes **8** and the corresponding chromium arene complexes **9**^a

8 R	C → D _h (°C)	D _h → I (°C)	9 C → N _D (°C)	N _D → I (°C)
a C ₅ H ₁₁	64	107	a —	125.2
b C ₆ H ₁₃	56	64	b —	85.6
c C ₇ H ₁₅	66	85	c —	67.3
d C ₈ H ₁₇	59	60	d —	46.4
e C ₉ H ₁₉	54	61	e 37.0	58.0
f C ₁₀ H ₂₁	57	67	f —	—

^aTransition temperatures of **8**, **9** were determined by DSC during first heating.

of thermotropic hexaalkoxy-substituted triphenylenes **4** [19] by complexation to a Cr(CO)₃ unit (Scheme 2). Of particular interest to us was the question, whether the metal fragment would disturb the hexagonal discotic alignment of triphenylenes **4** or not [20]. The results containing the synthesis and properties of novel arene complexes are described below.

2. Results and discussion

As shown in Scheme 3 triphenylenes **4** were synthesized via base-catalyzed etherification of brenzcatechine **6** [21], followed by an oxidative trimerization of **7** in aqueous sulfuric acid (70 vol.%) in the presence of FeCl₃ in moderate overall yields [22].⁴ Refluxing hexaalkoxytriphenylenes **8** with Cr(CO)₆ in Bu₂O/THF for several hours [27] resulted in the clean formation of chromium arene complexes **9** with the chromium tricarbonyl moiety being exclusively attached to one terminal alkoxy-substituted aryl ring. However, in the case of hexadecyloxytriphenylene **8f** an inseparable mixture of two chromium complexes was observed, presumably the monocoordinated compound **9f** and the corresponding internal chromium complex. The favored formation of the terminally coordinated arene complexes **9** is in complete accordance with observations by Deubzer et al. [28,29] Fischer and Öfele [30], and King and Stone [31]. They found that anellated aryl systems usually gave only monochromiumtricarbonyl complexes, in which the chromium fragment is coordinated to the aryl ring with the largest index of local aromaticity, i.e., the terminal, least anellated ring. Further support came from Sato, who reported that unsubstituted triphenylene pro-

⁴ Alternative syntheses of triphenylenes, see Refs. [23–26].

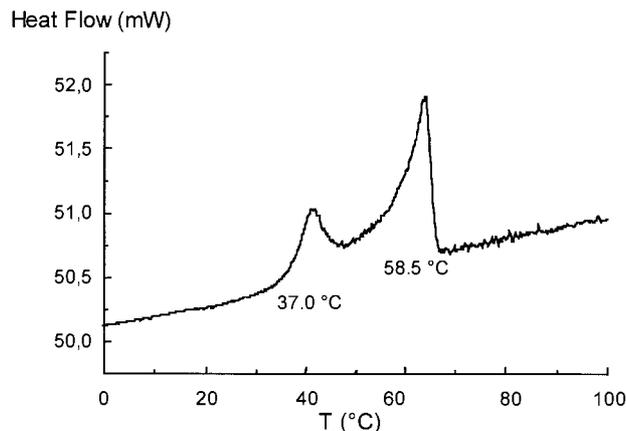
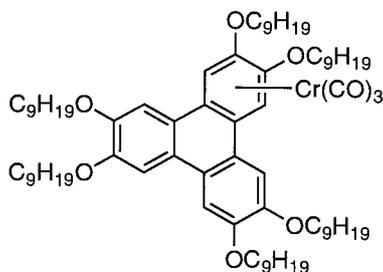


Fig. 1. Differential scanning calorimetry thermogram of **9e** registered during the first heating.

duced on treatment with $\text{Cr}(\text{CO})_6$ only the terminally coordinated arene complex [32,33].



The triphenylene chromium complexes **9** can be easily identified by ^1H NMR spectroscopy. Whereas the

signal for the six equivalent aromatic H's of the parent hexaalkoxytriphenylenes **8** appear at 7.80–8.15 ppm, the signals for 1-H, 4-H of the chromium arene complex **9** are shifted highfield towards 6.15–6.30 ppm. The signals of those hydrogens which are not directly attached to the chromium bearing aryl ring, i.e., 5-H, 12-H and 8-H, 9-H, respectively, display a much smaller highfield shift and can be observed at 7.55–7.75 ppm. A similar highfield shift was deduced from the ^{13}C NMR spectra. The signals for C-1 appeared at 73 ppm instead of 107 ppm for the uncomplexed derivative **8**, the signal for C-1a was observed at 95 ppm instead of 124 ppm and the signal for C-2 shifted from 149 ppm to 132 ppm.

The phase transition temperatures of triphenylene chromium complexes **9**, which were obtained by differential scanning calorimetry (DSC), are shown in Table 1. To avoid sample decomposition DSC analyses were recorded for one heating run only [18]. For comparison the phase transition temperatures of the corresponding metal free triphenylenes **8** are given as well [34]. The results show that the columnar stacking of the triphenylenes which leads to hexagonal discotic mesophases in compounds **8a–e** is severely disturbed by attachment of a chromium tricarbonyl moiety to the triphenylene system. Consequently the chromium complexes **9a–d** undergo a direct crystalline to isotropic phase transition at temperatures which are in a similar range as the $D_h \rightarrow I$ phase transition of the corresponding chromium free compounds **8a–d**. However, the hexanonyloxy triphenylene chromium complex **9e**

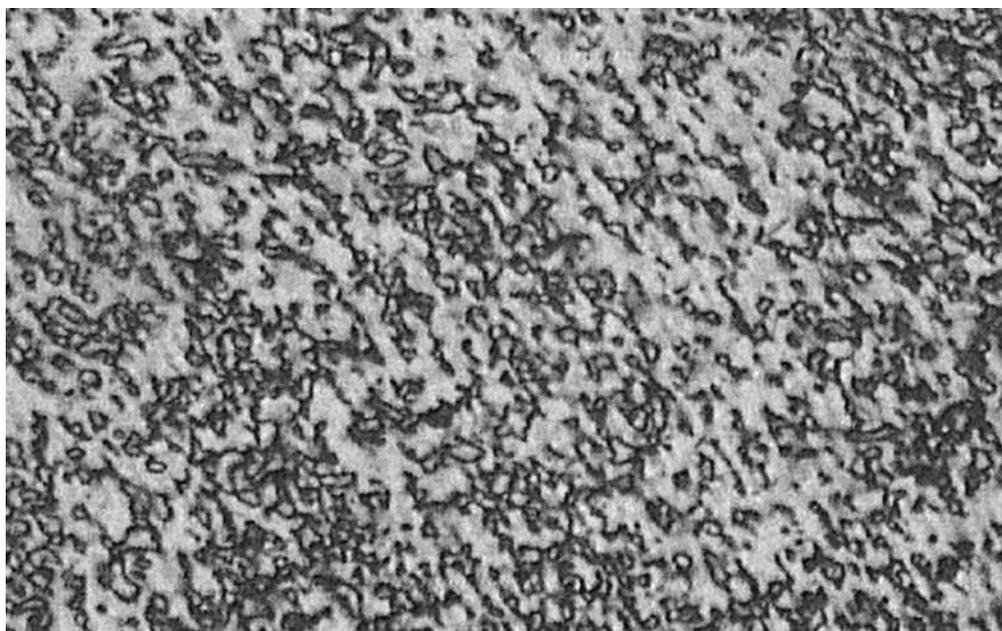


Fig. 2. Texture of a sample of **9e** between crossed polarizers at 50°C. Magnification: 250 × .

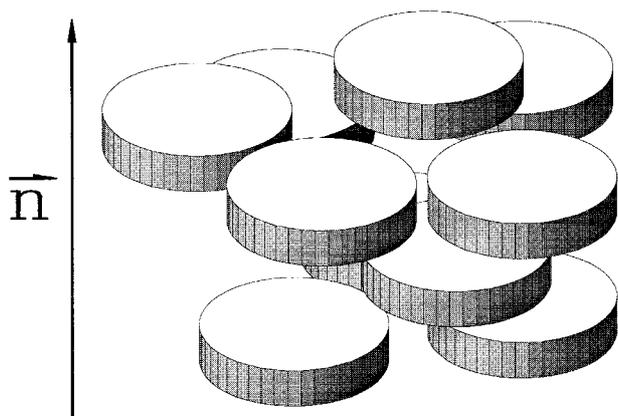


Fig. 3. Proposed nematic N_D structure of **9e**.

showed a different behavior.⁵ A $C \rightarrow M$ transition at 37°C was observed. On further heating, the mesophase was transformed into the isotropic phase at 58°C (Fig. 1). Optical polarizing microscopy revealed an unspecified texture at 50°C (Fig. 2), which is similar to marbled textures observed for nematic liquid crystals [35]. A symmetric cross was found, when **9e** was observed by conoscopy. This is characteristic for homeotropic uniaxial nematic textures [35–37]. X-ray diffraction experiments of non-ordered samples of **9e** were performed between 50° and 90°C. The X-ray diffraction pattern at 50°C exhibits two sharp reflexes at 22.7 Å and 16.5 Å respectively in the small angle region and a diffuse halo around 3.9 Å in the wide angle region. The most significant changes of the diffraction pattern occur in the small angle region. At about 60°C an additional peak at 20.5 Å appears, whose intensity increases during further heating, whereas the other peaks at 22.7 Å and 16.5 Å decrease and completely disappear at about 65°C.⁶ Based on these results we assigned the mesophase of **9e** as disk-like nematic N_D (Fig. 3). The different behavior of **9e** as compared to **8a–e** and **9a–d**, respectively, might be rationalized as follows. The columnar alignment of the triphenylene units, which was found in hexagonal discotic (D_h) phases of **8a–e**, is largely disfavored by the ‘non-symmetric’ complexation of the bulky chromium tricarbonyl moiety especially for shorter (C_5 – C_8) alkyl chains. For the C_9 derivative **9e** the influence of the alkyl chain on the molecular properties becomes more prominent.⁷ However, due to the bulkiness of the $Cr(CO)_3$ the nematic form of the discotic mesophase is favored against the standard columnar (D_h) mesophase [38,39].⁸

⁵ Deschenaux et al. reported a similar decrease of the mesophase stability for rod-like nematic chromium arene complexes as compared to the corresponding metal-free compounds. See Ref. [18].

⁶ Although compound **9e** could be sheared at 37–58°C, an X-ray diffraction of the ordered sample could not be obtained.

3. Conclusion

The synthesis of novel terminally coordinated (η^6 -hexaalkoxytriphenylene) $Cr(CO)_3$ complexes **9a–e** has been elaborated. DSC measurements revealed the strong influence of the metal fragment on the mesogenic properties. Whereas the parent uncomplexed triphenylenes **8a–e** display a D_h mesophase upon heating, only the hexanonyloxy-substituted complex **9e** showed a nematic N_D mesophase. Despite the limitations of the above described method, it seems reasonable that columnar mesophases might be achieved with other disk-shaped chromium arene complexes possessing a centrally bound $Cr(CO)_3$ moiety.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded on a Bruker AC 200 P (200 MHz 1H ; 50 MHz ^{13}C), a Bruker ARX 300 (300 MHz 1H ; 75 MHz ^{13}C), and a Varian Unity-plus (600 MHz 1H ; 150 MHz ^{13}C). The signals of H’s (and C’s), which are part of the chromium coordinated aryl ring, are marked with an * in the 1H (and ^{13}C) NMR spectra. IR spectra: DIGILAB FTS-45-FTIR spectrometer. Differential scanning calorimetry: Perkin Elmer 7 Series Thermal Analysis System, heating rate: 5°C min⁻¹, temperature range: –30° to +100°C under Ar. Mass spectra were obtained with a Finnigan Model MAT 312 spectrometer (ionization potential 70 eV). 1,2-Dialkoxybenzenes **7** were prepared according to Ref. [45] and 2,3,6,7,10,11-hexaalkoxytriphenylenes **8a–f** were prepared according to Ref. [22]. Optical polarizing microscopy: a Mettler FP 82 hot stage controlled by a Mettler FP 80 central processor was used together with a Leitz Ortholux II Pol-BK microscope. X-ray diffraction experiments were performed with monochromatic $CuK\alpha$ radiation ($\lambda = 1.54$ Å) using a two-dimensional image plate system (700 × 700 pixels).

⁷ The influence of the alkyl chain lengths on the molecular properties manifests itself also in the mass spectra of compounds **8**, **9**. The mass spectra of **8a–e** always show the M^+ peak as base peak and almost no fragmentation pattern. In the spectra of the corresponding chromium complexes **9a–c** (C_5 – C_7) the $[M^+ - Cr(CO)_3]$ peak appears as base peak. However, in the mass spectra of complexes **9d,e** (C_8, C_9) the $[M^+ - Cr(CO)_3]$ peak appears only with 65% rel. intensity (base peak m/z 56).

⁸ For related observations see Refs. [40–44].

4.1.1. General procedure for the preparation of triphenylene chromium arene complexes **9**

A solution of triphenylene **8** (2.69 mmol) and Cr(CO)₆ (3.55 g, 16.2 mmol) in Bu₂O/THF (10:1) was refluxed for 20 h under argon. After removal of the solvent in vacuo the remaining orange solid was heated for 1 h at 100°C (0.1 mbar). The crude product was recrystallized from EtOH.

4.1.2. 2,3,6,7,10,11-Hexapentyloxytriphenylene-(1,1a,2,3,4,4a)-tricarbonyl-chromium(0) **9a**

1.68 g (1.90 mmol, 71%) of yellow crystals; Mp 125.2°C; IR (KBr) 1945, 1872, 1843 cm⁻¹; ¹H NMR (600 MHz, C₆D₆) 7.64 (s, 2H, 5-H, 12-H), 7.63 (s, 2H, 8-H, 9-H), 6.21 (s, 2H, 1-H, 4-H), 4.22-3.93 (m, 12H, OCH₂CH₂, OCH₂CH₂^{*}), 1.88-1.72 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂CH₂^{*}), 1.54-1.32 (m, 24H), 0.93 (t, *J* = 9.1 Hz, 18H, CH₂CH₃, CH₂CH₃^{*}); ¹³C NMR (50 MHz, C₆D₆) 234.2 (CO), 151.1, 149.9 (C-6, C-7, C-10, C-11), 132.2, 125.0, 121.1 (C-2, C-3, C-5a, C-8a, C-9a, C-12a), 107.7, 107.5 (C-5, C-8, C-9, C-12), 95.2 (C-1a, C-4a), 73.6 (C-1, C-4), 71.1, 70.1, 69.3 (OCH₂, OCH₂^{*}), 29.6, 29.5, 28.8, 28.7, 28.6, 22.9 (CH₂), 14.3 (CH₃, CH₃^{*}); MS (EI) *m/z* 880 (M, 3), 799 (3), 798 (14), 796 (M-3 CO, 52), 747 (14), 744 (M-Cr(CO)₃, 100), 673 (6), 655 (14), 654 (22), 604 (4), 463 (8), 393 (5), 323 (7), 295 (6), 293 (2), 149 (7), 83 (3), 71 (10); HRMS calcd. for C₅₁H₇₂O₉Cr 880.4583, found 880.4560. Anal. Calcd. for C₅₁H₇₂O₉Cr: C, 69.52; H, 8.24. Found: C, 70.08; H, 8.26.

4.1.3. 2,3,6,7,10,11-Hexahexyloxytriphenylene-(1,1a,2,3,4,4a)-tricarbonyl-chromium(0) **9b**

2.30 g (2.38 mmol, 99%) of a yellow solid. Mp 85.6°C; IR (KBr) 1946, 1877, 1844 cm⁻¹; ¹H NMR (200 MHz, C₆D₆) 7.60 (s, 4H, 5-H, 8-H, 9-H, 12-H), 6.17 (s, 2H, 1-H, 4-H), 4.40-3.75 (m, 12H, OCH₂CH₂, OCH₂CH₂^{*}), 2.08-1.70 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂CH₂^{*}), 1.70-1.10 (m, 36H), 0.93 (s, 18H, CH₂CH₃, CH₂CH₃^{*}); ¹³C NMR (50 MHz, C₆D₆) 234.2 (CO), 151.0, 149.8 (C-6, C-7, C-10, C-11), 132.2, 124.9, 121.1 (C-2, C-3, C-5a, C-8a, C-9a, C-12a), 107.6, 107.5 (C-5, C-8, C-9, C-12), 95.2 (C-1a, C-4a), 73.6 (C-1, C-4), 71.1, 70.1, 69.3 (OCH₂, OCH₂^{*}), 32.1, 30.0, 29.8, 26.1, 26.2, 26.1, 23.0 (CH₂), 14.2 (CH₃, CH₃^{*}); MS(EI) *m/z* 964 (M, 6), 884 (6), 883 (20), 881 (M-3 CO, 64), 831 (20), 830 (62), 829 (M-Cr(CO)₃, 100), 711 (18), 710 (22), 659 (2), 491 (3), 440 (4), 149 (3), 97 (5), 84 (10), 69 (17), 60 (20), 57 (27); HRMS calcd. for C₅₇H₈₉O₉Cr 964.5522, found 964.5498. Anal. Calcd. for C₅₇H₈₉O₉Cr: C, 70.93; H, 8.77. Found: C, 71.06; H, 8.98.

4.1.4. 2,3,6,7,10,11-Hexaheptyloxytriphenylene-(1,1a,2,3,4,4a)-tricarbonyl-chromium(0) **9c**

1.80 g (1.72 mmol, 86%) of a yellow solid. Mp 67.3°C. IR (KBr) 1947, 1877, 1844 cm⁻¹; ¹H NMR

(200 MHz, C₆D₆) 7.74 (s, 2H, 5-H, 12-H), 7.71 (s, 2H, 8-H, 9-H), 6.31 (s, 2H, 1-H, 4-H), 4.28-3.87 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂^{*}), 2.00-1.62 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂CH₂^{*}), 1.60-1.10 (m, 48H), 0.93 (s, 18H, CH₂CH₃, CH₂CH₃^{*}); ¹³C NMR (75 MHz, C₆D₆) 234.2 (CO), 151.3, 150.1 (C-6, C-7, C-10, C-11), 132.3, 125.1, 121.9 (C-2, C-3, C-5a, C-8a, C-9a, C-12a), 107.9, 107.8 (C-5, C-8, C-9, C-12), 95.4 (C-1a, C-4a), 73.8 (C-1, C-4), 71.2, 70.2, 69.4 (OCH₂, OCH₂^{*}), 32.2, 30.0, 29.8, 29.6, 26.6, 26.5, 26.4, 23.0 (CH₂), 14.3 (CH₃, CH₃^{*}); MS(EI) *m/z* 1048 (M, 2), 966 (18), 965 (38), 964 (M-3 CO, 46), 915 (4), 914 (22), 913 (65), 912 (M-Cr(CO)₃, 100), 813 (6), 768 (4), 767 (12), 766 (18), 715 (2), 684 (3), 519 (3), 482 (4), 111 (4), 71 (16), 70 (28), 56 (49); HRMS calcd. for C₆₃H₉₆O₉Cr 1048.6461, found 1048.6430. Anal. Calcd. for C₆₃H₉₆O₉Cr: C, 72.10; H, 9.22. Found: C, 71.96; H, 9.21.

4.1.5. 2,3,6,7,10,11-Hexaoctyloxytriphenylene-(1,1a,2,3,4,4a)-tricarbonyl-chromium(0) **9d**

1.62 g (1.43 mmol, 71%) of an orange wax-like solid; Mp 46.4°C; IR (KBr) 1947, 1876, 1845 cm⁻¹; ¹H NMR (200 MHz, C₆D₆) 7.55 (s, 4H, 5-H, 8-H, 9-H, 12-H), 6.13 (s, 2H, 1-H, 4-H), 4.21-3.80 (m, 12H, OCH₂CH₂, OCH₂CH₂^{*}), 2.05-1.70 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂CH₂^{*}), 1.70-1.08 (m, 60H), 0.93 (s, 18H, CH₂CH₃, CH₂CH₃^{*}); ¹³C NMR (50 MHz, C₆D₆) 234.2 (CO), 151.0, 149.8 (C-6, C-7, C-10, C-11), 132.3, 124.8, 121.0 (C-2, C-3, C-5a, C-8a, C-9a, C-12a), 107.5 (C-5, C-8, C-9, C-12), 95.2 (C-1a, C-4a), 73.6 (C-1, C-4), 71.1, 70.1, 69.4 (OCH₂, OCH₂^{*}), 32.3, 30.0, 29.8, 26.8, 26.6, 23.1 (CH₂), 14.4 (CH₃, CH₃^{*}); MS(EI) *m/z* 1133 (M, 1), 1051 (4), 1050 (16), 1049 (M-3 CO, 30), 999 (6), 998 (48), 997 (M-Cr(CO)₃, 63), 884 (6), 882 (19), 742 (2), 741 (3), 525 (2), 524 (3), 114 (5), 112 (19), 83 (31), 71 (36), 70 (70), 56 (80), 55 (100); HRMS calcd. for C₆₉H₁₀₈O₉Cr 1132.7401, found 1132.7428. Anal. Calcd. for C₆₉H₁₀₈O₉Cr: C, 73.11; H, 9.60. Found: C, 73.16; H, 10.04.

4.1.6. 2,3,6,7,10,11-Hexanonyloxytriphenylene-(1,1a,2,3,4,4a)-tricarbonyl-chromium(0) **9e**

2.00 g (1.64 mmol, 89%) of an orange wax-like solid. Transition temperatures: C 37.0 [Δ*H* = 2.771 J/g]N_D 58.5 [Δ*H* = 10.02 J/g] I. IR (KBr) 1946, 1878, 1844 cm⁻¹; ¹H NMR (200 MHz, C₆D₆) 7.60 (s, 2H, 5-H, 12-H), 7.57 (s, 2H, 8-H, 9-H), 6.15 (s, 2H, 1-H, 4-H), 4.33-3.87 (m, 12H, OCH₂CH₂, OCH₂CH₂^{*}), 2.06-1.71 (m, 12H, OCH₂CH₂CH₂, OCH₂CH₂CH₂^{*}), 1.70-1.15 (m, 72H), 0.94 (s, 18H, CH₂CH₃, CH₂CH₃^{*}); ¹³C NMR (75 MHz, C₆D₆) 234.2 (CO), 151.0, 149.8 (C-6, C-7, C-10, C-11), 132.2, 124.9, 121.7 (C-2, C-3, C-5a, C-8a, C-9a, C-12a), 107.7, 107.5 (C-5, C-8, C-9, C-12), 95.1 (C-1a, C-4a), 73.6 (C-1, C-4), 71.1, 70.2,

69.4 (OCH₂, OCH₂^{*}), 32.4, 30.1, 29.9, 29.8, 26.8, 26.6, 23.1, 14.3 (CH₃, CH₃^{*}); MS(EI) *m/z* 1216 (M, 0.22), 1134 (6), 1133 (12), 1132 (M-3 CO, 16), 1083 (5), 1082 (22), 1081 (56), 1080 (M-Cr(CO)₃, 67), 1079 (7), 991 (1), 954 (6), 915 (2), 912 (8), 797 (3), 796 (5), 566 (2), 128 (4), 126 (12), 98 (16), 97 (22), 85 (28), 84 (28), 70 (58), 69 (49), 56 (100), 55 (90). HRMS calcd. for C₇₅H₁₂₀O₉Cr 1216.8340, found 1216.8312. Anal. Calcd. for C₇₅H₁₂₀O₉Cr: C, 73.97; H, 9.93. Found: C, 73.94; H, 10.18.

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